

## Title Page

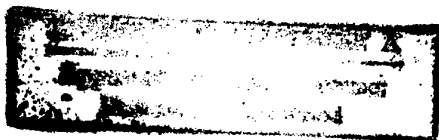
- (1) Title of Research Project: LIQUID CRYSTALLINE DENDRIMERS.
- (2) Name of Principal Investigator Valery P. Shibaev
- (3) Name of Contractor Valery P. Shibaev
- (4) Contract number № 68171-97-M-5822

(5) **FIRST INTERIM REPORT**

(6) November 1997 - December 1997

- (7) The Research reported in this document has been made possible through the support and sponsorship of the U.S. Government through its European Research Office of the U.S. Army. This report is intended only for the internal management use of the Contractor and U.S. Government.

19981006 103



<b>REPORT DOCUMENTATION PAGE</b>			Form Approved OMB No. 0704-0188	
Public reporting for this collection is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources gathering and maintaining the data needed and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204 Arlington, VA 22202-4302, and to the Office of Management and Budget Paperwork Reduction Project (0704-0188), m555 Paperwork Reduction				
1. AGENCY USE ONLY (Leave Blank)		2. REPORT DATE <b>30 June 1998</b>	3. REPORT TYPE AND DATES COVERED <b>1st interim report (November 1997 - December 1997)</b>	
4. TITLE AND SUBTITLE <b>LIQUID CRYSTALLINE DENDRIMERS. 1. Synthesis of five generations of carbosilane liquid crystalline dendrimers with terminal cyanobiphenyl groups.</b>			5. FUNDING NUMBERS <b>C N68171-97-M-5822 WU 1</b>	
6. AUTHOR(S) <b>V.P. Shibaev, N.I. Boiko, A.M. Muzafarov, E.A. Rebrov, S.A. Ponomarenko, S.A. Amelechina</b>				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>Chemistry Department, Moscow State University, Leninskiye Gory, GSP-3, 119899 Moscow, Russia</b>			8. PERFORMING ORGANIZATION REPORT NUMBER <b>MSU ERO C 11R/98</b>	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) <b>Pearse A. McDade, Naval Regional Contracting Center, Detachment London, Block2, wing11, DOE Complex, Eastcote Road Ruislip, Middx, UK, HA4 8BS</b>			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT <b>Distribution unlimited</b>			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words)  Using the controlled layer by layer experimental technique via reiterative sequence of chemical reactions carbosilane LC dendrimers with terminal cyanobiphenyl mesogenic groups of generations 1 – 5 were synthesized. Molecular structure and purity of all new compounds were characterized by <sup>1</sup> H-NMR spectroscopy and GPC analysis. Thermal behavior of LC dendrimers was investigated by means of polarizing optical microscopy and DSC methods. All LC dendrimers synthesized have mesophases of smectic types over wide temperature region. Values of glass transition temperatures of LC dendrimers do not depend on generation number, but isotropisation temperature raises with increasing of generation number of LC dendrimers. LC dendrimer of generation 5 bearing 128 cyanobiphenyl mesogenic groups displays unusual type of structural polymorphism, which is under investigation..				
14. SUBJECT ITEMS <b>Liquid Crystals, Dendrimers, Liquid Crystalline Dendrimers, Synthesis, Hydrosilation, Smectics, Cyanobiphenil Mesogenic Groups</b>			15. NUMBER OF PAGES <b>3</b>	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT <b>Unclassified</b>	18. SECURITY CLASSIFICATION OF THE THIS PAGE <b>Unclassified</b>	19. SECURITY CLASSIFICATION OF ABSTRACT <b>Unclassified</b>	20. LIMITATION OF ABSTRACT <b>UL</b>	

## BODY OF THE REPORT

### (1) The Scientific Work done during the reporting period.

Synthesis of liquid crystalline (LC) carbosilane dendrimers of generations 1 - 5 with 8, 16, 32, 64 and 128 terminal mesogenic groups was performed.

Firstly, carbosilane dendrimers with terminal allyl groups  $G-n(All)_m$  ( $n$  is the generation number;  $m$  is the number of terminal groups (allyl) shown in the parenthesis) were synthesized by divergent approach via Grignard/hydrosilylation reiterative stepwise technique. These dendrimers have four-functional central branching core and three-functional branching units leading to the degree of branching on the each step equal to two. In such a way for the first time the carbosilane dendrimers with 8, 16, 32, 64 and 128 terminal allyl groups, corresponding to generations 1, 2, 3, 4, and 5 have been synthesized respectively. Structure of all carbosilane dendrimers synthesized was confirmed by  $^1H$ -NMR spectroscopy. Purity and individuality of these compounds were approved by GPC analysis. All dendrimers synthesized are monodisperse individual substances with polydispersity less than 1.01.

Secondly, cyanobiphenyl mesogenic groups were modified in such a way that they have methylene spacer and active terminal groups Si-H capable of reacting with the terminal allyl groups of carbosilane dendrimers. Structure of all intermediates and final compounds were proved by  $^1H$ -NMR spectroscopy.

Finally, coupling of cyanobiphenyl mesogenic groups modified (H-Si-Und-CB) to the carbosilane dendrimers  $G-n(All)_m$  was carried out via hydrosilylation reaction in toluene solution in the presence of Pt-catalyst. Reactions were continued until allyl groups have disappeared completely. It was controlled by decreasing to zero of intensities of characteristic proton multiplets in the regions of  $\delta_1 = 4.80$  ppm and  $\delta_2 = 5.74$  ppm due to allyl carbon-carbon double bonds near Si atom in the  $^1H$ -NMR spectra. Molecular constitution and purity of all new compounds were characterized by  $^1H$ -NMR spectroscopy and GPC analysis.

Thermal behavior of LC dendrimers was investigated by means of polarizing optical microscopy and differential scanning calorimetry. All LC dendrimers synthesized have mesophases of smectic types over wide temperature region. Values of glass transition temperatures of LC dendrimers do not depend on generation number, but isotropisation temperature raises with increasing of generation number of LC dendrimers. There are no any significant changes of the phase behavior from first to third generations. These LC dendrimers form smectic A and smectic C mesophases. LC dendrimer of fifth generation has at least two new mesophases different from those of the previous generations. The structures of these mesophases are under study by X-ray measurements now.

No scientific meetings related to the Project were attended in this period.

Paper entitled «Synthesis of carbosilane liquid crystalline dendrimers of generations first to five, containing terminal cyanobiphenyl mesogenic groups» by S. Ponomarenko, N. Boiko, E. Rebrov, A. Muzafarov, V. Shibaev was submitted to the journal «Vysokomolekulyarnye soedineniya» (in Russian), «Polymer Science» (English translation).

Abstract for the poster presentation was submitted to 17<sup>th</sup> International Liquid Crystal Conference, which will be held in Strasbourg (France) on July 19-24 1998.

### (2) Research plans for remainder of the contract period

#### 1. Synthesis of LC dendrimers.

- a) Synthesis of at least five generations of carbosilane LC dendrimers with other (methoxyphenyl benzoate and cholesteryl) terminal mesogenic groups.
- b) Synthesis of LC dendrimers with different spacer length (3, 4, 5, 6 methylenic groups).
- c) Synthesis of LC dendritic statistical copolymers.

#### 2. Study of phase behavior and structure of all LC dendrimers by the optical polarizing microscopy, DSC and X-ray methods.

#### 3. Investigation of molecular properties of solutions of LC dendrimers.

### (3) During the reported period no significant administrative actions were made.

### (4)